

Rec'd PCT/PTC 16 JUL 2004

(12) DEMANDE INTERNATIONALE PUBLIÉE EN VERTU DU TRAITÉ DE COOPÉRATION EN MATIÈRE DE BREVETS (PCT)

(19) Organisation Mondiale de la Propriété Intellectuelle

Bureau international



(43) Date de la publication internationale 31 juillet 2003 (31.07.2003)

PCT

(10) Numéro de publication internationale WO 03/061878 A2

- (51) Classification internationale des brevets⁷: B22D 13/10
- (21) Numéro de la demande internationale :

PCT/FR03/00181

(22) Date de dépôt international :

21 janvier 2003 (21.01.2003)

(25) Langue de dépôt :

français

(26) Langue de publication :

français

(30) Données relatives à la priorité : 02/00947 25 janvier 2002 (25.01.2002) FF

- (71) Déposant (pour tous les États désignés sauf US):
 PECHINEY ELECTROMETALLURGIE [FR/FR];
 235, avenue Alsace Lorraine, F-73000 Chambéry (FR).
- (72) Inventeur; et
- (75) Inventeur/Déposant (pour US seulement): MAR-GARIA, Thomas [FR/FR]; 45, impasse des Clos de Bouan, F-74190 Passy (FR).
- (74) Mandataire: PECHINEY; Jean-ClaudeMougeot, 217, Cours Lafayette, F-69451 Lyon Cedex 06 (FR).

- (81) États désignés (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) États désignés (régional): brevet ARIPO (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), brevet eurasien (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), brevet européen (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), brevet OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Déclaration en vertu de la règle 4.17 :

 relative à la qualité d'inventeur (règle 4.17.iv)) pour US seulement

Publiée:

 sans rapport de recherche internationale, sera republiée dès réception de ce rapport

En ce qui concerne les codes à deux lettres et autres abréviations, se référer aux "Notes explicatives relatives aux codes et abréviations" figurant au début de chaque numéro ordinaire de la Gazette du PCT.

- (54) Title: PRODUCTS FOR THE PROTECTION OF CONTINUOUS CAST MOULDS FOR CAST-IRON PIPES
- (54) Titre: PRODUITS POUR LA PROTECTION DES MOULES DE COULEE CONTINUE DES TUYAUX DE FONTE
- (57) <u>Abstract:</u> The invention relates to a powder which is used to protect spin cast moulds for cast-iron pipes. The inventive product comprises: an inoculant metal alloy; optionally, mineral powders; and a metal which is highly reducing and volatile at the temperature of the liquid iron. According to the invention, the use of said products prevents mould fouling and improves the surface condition of cast-iron pipes.
- (57) Abrégé: L'invention a pour objet un produit en poudre pour la protection des moules de coulée centrifugée des tuyaux de fonte, comprenant un alliage métallique inoculant et éventuellement des poudres minérales, ainsi qu'un métal fortement réducteur et volatil à la température de la fonte liquide. L'utilisation des produits selon l'invention évite l'encrassement des moules et améliore l'état de surface des tuyaux de fonte.



PRODUCTS FOR THE PROTECTION OF CONTINUOUS CASTING MOULDS FOR CAST IRON PIPES

Field of the invention

The invention relates to a powder product designed to protect casting moulds for cast iron pipes made by centrifugal casting; the casting moulds used are commonly referred to as "shells".

5

10

15

20

25

State of the art

Coatings used for protection of centrifugal casting shells for cast iron pipes were composed firstly of inoculation products and powder refractory materials, and mixes of silica and bentonite placed by spraying of an aqueous solution. For example, this type of coating is described in Pont-à-Mousson's US patent 4 058 153.

These products were subsequently replaced by dry spray powders sprayed on the shell before the cast iron was moulded, using the technique referred to as "dry spray". Regardless of the technique used for their placement, these products are used to create a thermal barrier effect limiting the temperature rise of the shell and thus contributing to increasing its life, and also an inoculating effect on the poured cast iron to control the metallurgical structure of the pipe.

It is well known that insufficient inoculation will lead to the formation of carbide in the cast iron, high shrinkage during cooling and fast mould stripping, which helps to increase productivity. But the parts thus obtained will require subsequent heat treatment that may be expensive.

Depending on the case, it may be preferred to inoculate more to prevent the final heat treatment even though the production rate is lowered, or on the other hand to inoculate only slightly to increase productivity and then apply heat treatment to the cast iron part.

Therefore, the inoculating power of the dry spray may vary within fairly wide limits, however other effects requested from the product are subjected to more constant requirements.

Therefore, dry spray products are usually composed of a mix of several components, including an inoculant with a variable efficiency that may form 30 to 100% of the product, for example a ferro-silicon containing 0.1 to 3% of aluminium and calcium and an inert mineral filler, for example silica or fluorspar that may form between 0 to 70% of the product.

Patent FR 2612097 (Foseco) describes the use of FeSiMg type alloys as treatment agents, with particles electrically charged by friction.

These mixes are in the form of powders with size grading always smaller than 400 μm , but free of fines. For example, a size grading of between 50 and 200 μm is well adapted.

25

30

5

10

15

20

Purpose of the invention

The purpose of the invention is a powder product for the protection of centrifugal casting moulds for cast iron pipes, comprising an inoculating metal alloy and possibly inert mineral powders and a highly reducing metal that is volatile at the temperature of the liquid cast iron.

Description of the invention

5

10

Products according to prior art used as dry spray for the manufacture of cast iron pipes by centrifugal casting have some disadvantages. The inert mineral filler added to the mix contributes to increasing the risks of making moulds dirty and the formation of inert mineral inclusions in the cast iron that can appear as surface defects on the pipes.

Furthermore, the applicant has observed that although the addition of a strongly reducing agent such as aluminium protects the shells and their life, in some cases, it can increase the risk of occurrence of unacceptable pitting defects on the surface of the pipes.

Therefore, the applicant's objective 15 develop products that protect the user from these disadvantages. These products comprise an inoculating alloy, for example based on ferro-silicon, or a mix of inoculating alloys, possibly a mineral filler and a reducing agent with a content of between 0.3 and 18%, 20 composed of a metal that is volatile at the temperature of the liquid cast iron, that may be a metal from Mendeleiev classification, 2 in the and column preferably a metal from column 2a in the periodic table of the elements. The preferred metals are calcium or 25 magnesium or alloys containing at least one of these Silicon alloys are particularly suitable, metals. particularly the CaSi alloys. Thus, the following alloy compositions can be used (by weight):

30 Si 58 - 65%; Ca 27 - 35%; Fe 2 - 7%; Al 0.4 - 2%.

The product preferably contains,

- either between 0.3 and 4% by weight of magnesium, and preferably between 0.5 and 2%. found that the casting mould starts to get dirty in the form of whitish traces of MgO if the content is higher than 4%.
- or 15 to 40% by weight of CaSi representing a calcium content of between 4 and 14%.

Tests carried out by the applicant have shown that ferrous alloys of the FeSiCa type, typically containing more than 10% iron and frequently called "CaSiFer" containing (by weight):

10

30

Si 51 - 58%; Ca 16 - 20%; Fe 23 - 27%; A1 0.3 -1.5%

and FeSiMg type alloys containing (by weight):

15 Si 47 - 53%; Fe 35 - 48%; Mg 2 - 12%; Al 0.2 -1.5%; Ca 0.1 - 1.5%, rare earths 0 - 2%,

give disappointing results, well below the results obtained with mixes according to the invention.

corresponding quantities of the different 20 constituents in the final mix were evaluated as a function of the defects that can arise as a result of overdoses.

Furthermore, for safety reasons related preparation of the products, the reducing metals or 25. reducing alloys are not used alone, but rather in the form of a premix with an inert substance, preferably calcium fluoride, magnesium fluoride or a mix of these two fluorides. For maximum efficiency, the strongly reducing metal alloy content in the premix preferably between 15 and 60%.

The size grading of the products is less than 400 μm, and is preferably less than 250 μm. Fine particles smaller than 40 μm and preferably smaller than 50 μm are excluded to prevent dust emission during use.

Examples

5

15

25

30

Example No. 1

A mix was prepared according to prior art with the following constituents:

85% ferro-silicon with 75.2% of Si, 1.3% of Ca and 0.45% of Al, with size grading of between 50 and 200 μm and 15% of fluorspar with a size grading of between 10 and 150 μm .

This product gave satisfactory results when used as a dry spray as a reference test; the pipes were stripped after 55 seconds of cooling and the thickness of ferritic cast iron measured on pipes made in this way was 35 microns. However, the shells were slightly attacked.

20 Example No. 2

A mix according to the invention was prepared from the following constituents:

55% ferro-silicon with 75.2% of Si, 1.3% of Ca and 0.45% of Al with size grading between 50 and 200 μ m and 45% of a mix composed of 1/3 fluorspar between 10 and 150 μ m, and 2/3 of calcium silicide with 60.1% of Si, 31.7% of Ca and 4.3% of Fe.

When used as a dry spray this product gave satisfactory results; the pipes were stripped after 45 seconds cooling and a thickness of 25 μ m of ferritic cast iron was measured on the pipes made in this way. However, there was no visible attack of the shells.

Therefore, this type of product gives better results than the product mentioned in example No. 1.

Example No. 3

A mix of 50% of magnesium powder with size grading between 50 and 250 μm , 25% of magnesium fluoride with size grading between 40 and 250 μm , and 25% fluorspar with size grading between 40 and 250 μm , was prepared.

A mix according to the invention was then prepared consisting of 3% of the previous mix and 97% of ferrosilicon with 75.2% of Si, 1.3% of Ca and 0.45% of Al with a size grading between 50 and 200 μ m.

When used as dry spray test, this product gave results considered to be better than those obtained in examples No. 1 and No. 2; the pipes were stripped after 37 seconds cooling and the pipes thus made were found to have a ferritic cast iron thickness of 30 μm . The surface condition of the parts was considered to be excellent.

20

5

10

15

Example No. 4

A mix according to prior art was prepared with an equivalent composition of the mix in example 3, composed (by weight) as follows:

- -43% of ferro-silicon with 75.2% of Si, 1.3% of Ca and 0.45% of Al with size grading between 50 and 200 μ m and originating from the same batch as the ferro-silicon used in the previous example.
- 29.5% of a FeSiMg type alloy with size grading between 50 and 200 μ m, analysed to contain 50.7% of Si, 42.0% of iron, 5.2% of Mg, 1.2% of Ca and 0.35% of Al,
 - 26% of metallurgical silicon powder with size grading between 50 and 200 μm containing 98.6% of Si.

- 0.75% of magnesium fluoride with size grading between 40 and 250 $\mu\text{m},$
- 0.75% of fluorspar with size grading between 40 and 250 μm_{\star}

When used as a dry spray, this product gave results significantly worse than those obtained in example 3. Pipes were stripped after 50 seconds cooling, the observed thickness of ferritic cast iron on the pipes thus made was 35 μ m, and absolutely unacceptable pitting was observed on the surface of the parts with a density of the order of 25 per m².